Perfluorinated Chemicals in Surface Waters and Sediments from Northwest Georgia, USA, and Their Bioaccumulation in *Lumbriculus variegatus*

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ABSTRACT

Concentrations of perfluorinated chemicals (PFCs) were measured in surface waters and sediments from the Coosa River watershed to examine their distribution downstream of a suspected source. Samples from eight sites were analyzed using liquid chromatography-tandem mass spectrometry. To examine PFC bioaccumulation, sediments were also utilized in 28-d exposures with the aquatic oligochaete, *Lumbriculus variegatus*. Concentrations increased significantly below a land-application site (LAS) of municipal/industrial wastewater and were further elevated by unknown sources downstream. Comparisons with past surveys indicate improving conditions, but additional information is needed. Perfluorinated carboxylic acids (PFCAs) with eight or less carbons were the most prominent in surface waters. Those with 10 or more carbons predominated sediment and tissue samples. Perfluorooctane sulfonate (PFOS) was the major homologue in contaminated sediments and tissues followed by perfluorodecanoate, perfluoroundecanoate, perfluorododecanoate, perfluorotridecanoate, and perfluorotetradecanoate. This pattern of sediment PFCs was consistent among sites and reflected homologue concentrations emanating from the LAS. Tissue PFC concentrations repeated patterns observed in the respective sediments but were 4 to 46 times greater depending on the homologue. The tendency to bioaccumulate increased with PFCA chain length and the presence of the sulfonate moiety. Bioaccumulation factors indicated that short-chain PFCAs with less than seven carbons may be environmentally benign alternatives in aquatic ecosystems, but sulfonates with four to seven carbons may be as likely to bioaccumulate as PFOS.

INTRODUCTION

Perfluorinated chemicals (PFCs) are a class of compounds widely used in commercial and industrial applications for over 50 years because of properties that include water, soil, and oil repellency. A variety of PFC homologues have been utilized that are differentiated by the number of carbons in the structure and by either a carboxylate (perfluorinated carboxylic acid, PFCA) or a sulfonate (perfluorinated sulfonic acid, PFSA) moiety attached to one end. The most common homologues found in environmental samples contain eight carbons (C8), perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA), which also tend to be the most effective surfactants [1]. In the United States, use and production of PFOS was substantially reduced after 2002 because of its increasing occurrence in human tissues (http://www.epa.gov/oppt/existingchemicals/pubs/pfcs_action_plan1230_09.pdf). The integration of PFCs into aquatic food webs can occur in systems containing fairly low PFC concentrations [2], but there is little known about the potential environmental effects associated with continual inputs of relatively high PFC concentrations. The bioaccumulation of six PFCs was documented in exposures to natural sediments with low concentrations [3], but no information is available concerning the bioaccumulation of a wide range of PFCs from highly-contaminated natural sediments.

The carpet industry, which is prevalent in northern Georgia, is suspected of producing wastewaters containing PFCs and PFC-precursor chemicals which are used in carpet-protection products. Effluents from multiple carpet manufacturers in the Dalton area are processed through a municipal wastewater-treatment plant which, in turn, sprays the treated effluent onto a land-application site (LAS) bordering the Conasauga River. A recent analysis of surface-water samples collected immediately above and below the site revealed high concentrations of selected PFCs downstream of the LAS [4]. Analyses of sediment samples collected in 2006 from their downstream site also indicated significant PFC contamination. Concentrations of PFHxA, PFHpA, PFOA, PFNA and PFDA were 1.12, 0.81, 4.56, 2.32, and 10.15 ng/g dw, respectively. The present study examined the concentrations of fifteen PFCs in surface waters and sediments upstream and downstream of the LAS and demonstrated their bioaccumulation from sediments into the freshwater oligochaete, *Lumbriculus variegatus*.

MATERIALS AND METHODS

- Three replicate samples of surface waters and sediments collected from eight locations during summer of 2008 (**Figure 1**)
- Bioaccumulation from sediment exposures determined using established procedures [5] with *Lumbriculus variegatus*
  - 3-L polycarbonate chamber, 1 L of sediment, 2 L of overlying water
  - 28-d exposures, 23ºC, 50% exchange of overlying water 3 times per day
  - Bioaccumulation rate ($BSAF_m$) described by ([tissue]/([sediment][sediment organic C]))
- PFC analyses (**Table 1**)
  - Sediment extracted four times with 60:40 acetonitrile:water (v:v); tissue extracted with ion-pairing procedure
  - Ultra-high-pressure liquid chromatography with tandem mass-spectrometry
  - Method detection limits
    - 0.005 to 0.028 ng/g for surface waters
    - 0.023 to 0.297 ng/g (dry weight) for sediments
    - 0.023 to 0.174 ng/g (wet weight) for tissues
  - Recoveries of internal standards
    - Sediments (71 to 92%); tissues (65 to 124%)
  - Homologue concentrations below MDLs in all blank water, sediment, and tissue samples
- Additional sediment analyses - metals, particle-size distribution, organic material, C, N

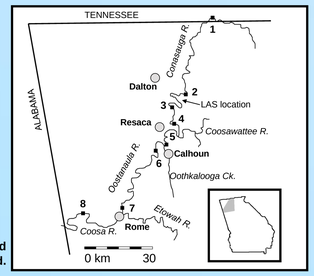

Figure 1. Collection sites for surface waters and sediments in the Coosa River watershed.

Table 1. PFC homologues analyzed in surface waters, sediments, and tissues.

Acronym	Name	Functional group	Number of carbons
Perfluorinated carboxylic acids (PFCAs)			
PFBA	Perfluorobutanoate	Carboxylate	4
PFPA	Perfluoropentanoate	Carboxylate	5
PFHxA	Perfluorohexanoate	Carboxylate	6
PFHpA	Perfluorheptanoate	Carboxylate	7
PFOA	Perfluorooctanoate	Carboxylate	8
PFNA	Perfluorononanoate	Carboxylate	9
PFDA	Perfluorodecanoate	Carboxylate	10
PFUnDA	Perfluoroundecanoate	Carboxylate	11
PFDoDA	Perfluorododecanoate	Carboxylate	12
PFTrDA	Perfluorotridecanoate	Carboxylate	13
PFTeDA	Perfluorotetradecanoate	Carboxylate	14
Perfluorinated sulfonic acids (PFSAs)			
PFBS	Perflourobutane sulfonate	Sulfonate	4
PFHxS	Perfluorohexane sulfonate	Sulfonate	6
PFHpS	Perfluoroheptane sulfonate	Sulfonate	7
PFOS	Perfluorooctane sulfonate	Sulfonate	8

RESULTS

- Significant PFC contamination of surface waters and sediments of the Conasauga and Oostanaula Rivers downstream of LAS (**Figure 2, Tables 2 and 3**)
- Total PFCA concentrations in surface waters greater than total PFSA concentrations at each site, but individually PFOS and PFBS present in the greatest concentrations followed by PFOA
- PFCAs with >10 carbons (PFUnDA, PFDoDA, PFTrDA, PFTeDA) below detection limits in all water samples
- Total PFCA concentrations in sediments were greater than total PFSA concentrations, but PFOS was the predominant homologue (1.5 to 4 times that of the highest PFCA)
- Sediment PFCA concentrations dominated by homologues with > 9 carbons
- Oligochaetes bioaccumulated PFCs from sediments collected from all eight sites
- Tissue concentrations greatest in samples from downstream of the LAS (**Figure 2, Table 4**)
- PFOS was the dominant homologue measured in tissues followed by PFCAs with > 9 carbons
- Bioaccumulation rate increased for PFCAs as the number of carbons increased (**Figure 3**)
- Bioaccumulation rates similar for PFSAs (PFBS, PFHxS, PFHpS, and PFOS)

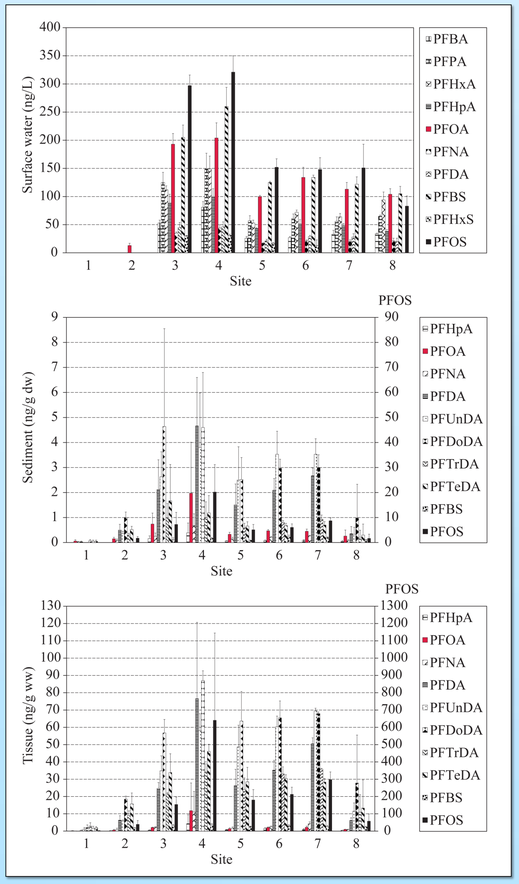

Figure 2. Mean concentrations of perfluorinated chemicals (plus 1 standard deviation, n = 3) in surface waters and sediments collected from eight sites heading downstream in the Conasauga, Oostanaula and Coosa Rivers, and in *Lumbriculus variegatus* tissues exposed to the collected sediments for 28 days. Sediment and tissue concentrations of PFOS are represented on the right axis.

Conasauga River

Table 2. Mean concentrations (ng/L) of perfluorinated chemicals (with coefficient of variation, n = 3) in surface waters collected from sites along the Conasauga, Oostanaula and Coosa Rivers.

	Site							
Homologue	1	2	3	4	5	6	7	8
PFBA	< MDL	< MDL	53ª (9)	81ª (12)	26ª (12)	27ª (6)	33ª (21)	34ª (2)
PFPA	< MDL	< MDL	125ª (15)	149ª (18)	57ª (15)	61ª (12)	56ª (14)	65ª (2)
PFHxA	< MDL	< MDL	112ª (6)	149ª (16)	53ª (8)	72ª (5)	64ª (10)	94ª (14)
PFHpA	< MDL	< MDL	89ª (16)	100ª (14)	43ª (4)	51ª (15)	48ª (8)	38ª (8)
PFOA	< MDL	13 (28)	193ª (10)	204ª (13)	100ª (2)	134ª (14)	113ª (10)	104ª (9)
PFNA	< MDL	< MDL	35ª (5)	44ª (14)	17ª (3)	21ª (8)	20ª (16)	21ª (22)
PFDA	< MDL	< MDL	45ª (20)	46ª (19)	21ª (16)	29ª (5)	28ª (20)	20ª (28)
PFBS	< MDL	< MDL	205ª (11)	260ª (7)	125ª (1)	134ª (3)	122ª (10)	105ª (12)
PFHxS	< MDL	< MDL	30ª (4)	31ª (7)	17ª (7)	13ª (45)	< MDL	<MDL
PFHpS	< MDL	< MDL	< MDL	< MDL	< MDL	< MDL	< MDL	< MDL
PFOS	< MDL	< MDL	297ª (6)	321ª (9)	152ª (10)	148ª (14)	151ª (28)	83ª (22)

*Concentration is significantly greater than those measured at sites 1 and 2 (Dunnett's one-tailed test, α ≤ 0.05). MDL = method detection limit.

Table 3. Mean concentrations (ng/g, dw) of perfluorinated chemicals (with coefficient of variation, n = 3) in sediments collected from sites along the Conasauga, Oostanaula and Coosa Rivers.

	Site							
Homologue	1	2	3	4	5	6	7	8
PFHxA	< MDL	< MDL	0.15 (100)	0.40 (128)	< MDL	< MDL	< MDL	< MDL
PFHpA	< MDL	< MDL	0.16 (70)	0.39[b] (100)	0.07 (18)	0.08 (18)	0.09 (27)	0.04 (101)
PFOA	0.06 (82)	0.15 (43)	0.74 (59)	1.97[b] (104)	0.33 (26)	0.47 (12)	0.45 (20)	0.26 (95)
PFNA	0.03 (62)	0.08 (76)	0.25 (50)	0.68[b] (69)	0.14 (53)	0.21 (12)	0.27 (8)	0.07 (75)
PFDA	0.03 (100)	0.50 (46)	2.12[a] (56)	4.66[b] (42)	1.51 (55)	2.09[a] (22)	2.67[b] (12)	0.35 (82)
PFUnDA	< MDL	0.36 (26)	2.63[b] (38)	3.80[b] (58)	2.50[a] (53)	3.53[b] (26)	3.53[b] (17)	0.33 (87)
PFDoDA	< MDL	1.00 (22)	4.64[b] (84)	4.60[b] (48)	2.52 (35)	2.97 (12)	3.00 (17)	0.98 (138)
PFTrDA	0.07 (75)	0.30 (22)	0.98[a] (59)	0.99[a] (65)	0.59 (31)	0.80[a] (10)	0.93[a] (19)	0.21 (139)
PFTeDA	0.05 (102)	0.52 (26)	1.67[a] (87)	1.19 (58)	0.66 (25)	0.68 (13)	0.70 (20)	0.30 (148)
PFBS	0.05 (87)	< MDL	.11 (73	0.17[b] (16)	0.09 (14)	0.22[c] (38)	0.26[b] (15)	0.10 (16)
PFHxS	< MDL	< MDL	0.07 (83)	0.17[b] (92)	< MDL	< MDL	< MDL	< MDL
PFHpS	< MDL	< MDL	< MDL	< MDL	< MDL	< MDL	< MDL	< MDL
PFOS	< MDL	1.73 (39)	7.24 (67)	20.18[b] (54)	5.10 (42)	6.05 (24)	8.70 (14)	1.66 (103)

[a] Concentration is significantly greater than measured at site 1; [b] Concentration is significantly greater than measured at sites 1 and 2 (Dunnett's one-tailed test, α ≤ 0.05). MDL = method detection limit.

Table 4. Mean concentrations (ng/g, ww) of perfluorinated chemicals (with coefficient of variation, n = 3) in tissues of *Lumbriculus variegatus* exposed to sediments collected from sites along the Conasauga, Oostanaula and Coosa Rivers.

	Site							
Homologue	1	2	3	4	5	6	7	8
PFHxA	< MDL	< MDL	0.37 (14)	1.31 (125)	0.26 (34)	0.19 (74)	0.30 (34)	0.29 (63)
PFHpA	0.16 (59)	0.30 (19)	0.52 (31)	4.29[b] (120)	0.75 (27)	1.58 (26)	0.95 (55)	0.32 (74)
PFOA	0.10 (69)	0.60 (67)	2.06 (11)	11.80 (136)	1.35 (39)	2.11 (13)	2.19 (30)	0.95 (13)
PFNA	< MDL	0.82 (103)	2.28 (7)	11.04[b] (108)	1.68 (44)	2.61 (12)	4.29 (24)	0.90 (15)
PFDA	0.35 (82)	6.36 (40)	24.71 (14)	76.58[b] (58)	26.28 (36)	35.28[a] (16)	50.44[b] (7)	6.10 (27)
PFUnDA	1.13 (85)	5.79 (12)	34.87[a] (25)	58.09[b] (17)	48.63[b] (26)	60.34[b] (10)	69.42[b] (2)	11.50 (42)
PFDoDA	2.00 (80)	18.47 (9)	56.77[b] (14)	87.02[b] (7)	63.62[b] (27)	65.48[b] (15)	67.92[b] (1)	27.78 (100)
PFTrDA	2.90 (67)	8.90 (32)	21.52[a] (4)	34.15[b] (14)	24.10[b] (28)	33.04[b] (12)	33.81[b] (1)	10.98 (92)
PFTeDA	1.55 (81)	15.74 (40)	33.86[b] (32)	46.06[b] (9)	28.49[a] (29)	30.40[a] (7)	28.34[a] (7)	13.30 (122)
PFBS	1.91 (37)	1.66 (28)	3.30[b] (15)	3.52[b] (25)	2.61 (11)	3.03[b] (22)	2.63 (22)	2.36 (17)
PFHxS	5.01 (63)	4.16 (44)	2.89 (33)	12.21[a] (43)	9.72 (21)	13.87[b] (43)	8.30 (50)	5.34 (69)
PFHpS	0.15 (117)	0.29 (145)	2.39 (8)	19.31[b] (132)	1.95 (35)	2.66 (8)	3.30 (38)	1.04 (130)
PFOS	1.61 (91)	39.15 (56)	154.18 (28)	640.55[b] (79)	179.89 (33)	212.54 (19)	297.29 (15)	57.36 (73)

[a] Concentration is significantly greater than measured at site 1; [b] Concentration is significantly greater than measured at sites 1 and 2;
[c] Concentration is significantly greater than measured at site 2 (Dunnett's one-tailed test, α ≤ 0.05). MDL = method detection limit.

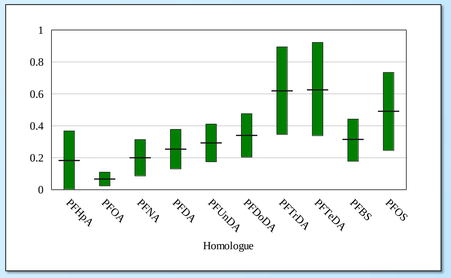

Figure 3. Mean modified biota-sediment accumulation factors ($BSAF_m$) +/- 1 standard deviation (n = 18) based on concentrations of perfluorinated chemicals in sediments and exposed oligochaetes.

DISCUSSION

- Carpet-industry effluents produced in the Dalton area contribute significant amounts of PFCs to the Conasauga and Oostanaula Rivers.
- Despite increasing discharge, concentrations of PFCAs and PFBS increased and PFOS concentrations remained steady as the river passed the cities of Resaca and Calhoun indicating sources of PFC contamination from this area as well.
- PFOS exceeded USEPA Provisional Health Advisory for drinking water (200 ng/L) at sites 3 and 4 (one replicate from site 7 with 199 ng/L). PFOA below Provisional Health Advisory (400 ng/L).
- PFC concentrations in surface waters have generally decreased since 2006 (**Table 5**), but are high in comparison with concentrations reported in the literature.
- Differences between water and sediment concentrations suggest that long-chain PFCAs sorb out of the dissolved phase quickly and are transported downstream as part of the sediment load.
- PFCA concentrations in sediments from sites downstream of the LAS indicated the same general pattern among homologues where PFDA, PFUnDA, and PFDoDA were most prominent followed by PFTrDA and PFTeDA (**Figure 2**). This pattern is similar to those determined in aged compost and sludge produced at the Dalton waste-treatment facility when the homologues that tend to stay in solution (PFOA, PFBS, PFCAs with 7 or less carbons) are excluded (**Table 6**).
- PFOS was the dominant homologue in water, sediment and tissue samples despite the phase out of PFOS production and use that began in 2003. However, a number of sulfonamide chemicals (PFOS precursors) are currently components of effluents permitted for discharge to the system.
- Conversely, low to non-detectable concentrations of fluorotelomer alcohols (PFCA precursors) indicate observed PFCAs were original components of wastewaters.
- Bioaccumulation of PFCs by *L. variegatus* indicated that all sites were contaminated; homologues with sediment concentrations below detection limits were accumulated to detectable levels in tissues.
- Bioaccumulation reflected the pattern in sediment PFC concentrations and also demonstrated the influence of increasing chain-length (number of carbons) on accumulation (**Figure 2, Figure 3**).

Table 5. Temporal comparison of concentrations (ng/L) of perfluorinated chemicals in surface waters sampled at site 3.

Homologue	Spring 2006[1]	Fall 2006[2]	Summer 2008[3]	2009[4]
PFBA		72	53	35
PFPA		242	125	138
PFHxA		193	112	109
PFHpA		182	89	66
PFOA	1,150	394	193	205
PFNA	284	102	35	35
PFDA	30	115	45	47
PFUnA	99	16	<MDL	
PFDoA		3	<MDL	
PFBS		288	205	252
PFOS	1	664	297	426

[1]Konwick et al., 2008; [2]United Steel Workers Union, (http://media.timesfreepress.com/docs/2008/03/3_18%20_DALTON%20EPA%20LETTER-%20Final.pdf); [3]present study; [4] Dalton Utilities, (www.epa.gov/region4/water/PFCdaltonindex.html). MDL = method detection limit.

Table 6. Concentrations (ng/g, dw) of perfluorinated chemicals in compost (mean, n=18) and sludge (Loopers Bend facility) produced by the Dalton Utility Department*.

Homologue	Compost	Sludge
PFBA	106	152
PFPA	143	415
PFHxA	219	190
PFHpA	216	338
PFOA	1521	134
PFNA	376	48
PFDA	1733	208
PFUnDA	896	347
PFDoDA	361	74
PFTrDA	273	195
PFTeDA	56	0
PFBS	794	1940
PFOS	409	170

*www.epa.gov/region4/water/PFCdaltonindex.html. Homologues that tend to stay in solution.

CONCLUSIONS

The LAS associated with the Dalton municipal waste treatment facility has contributed significant amounts of PFCs to the Conasauga and Oostanaula Rivers, and there appear to be additional sources of PFCs downstream. Concentrations of PFCs measured in surface-water and sediment samples were high compared to other contaminated sites reported in the literature. Despite reductions in PFOS production and use, it was the dominant PFC measured in samples collected for this study and continues to pose a potential risk to biota in the watershed. However, PFOS concentrations may be remaining elevated due to transformations of PFOS-precursor chemicals that continue to be discharged at the LAS. Low to non-detectable concentrations of fluorotelomer alcohols were observed in these samples indicating that the PFCAs present were originally components of wastewater discharges. Concentrations of PFCs may be decreasing based on comparisons with past surveys, but periodic monitoring of surface waters and sediments will be required to determine long-term trends. After exposure to the sediments, PFOS and PFCAs with ten or more carbons were present in the greatest concentrations within oligochaete tissues. Bioaccumulation of PFSAs and PFCAs by *L. variegatus* appeared to be primarily related to sediment concentrations, but the tendency among PFCs to bioaccumulate increased with chain length and the presence of the sulfonate moiety. Short-chain PFCAs may be viable alternatives to the longer-chain PFCAs, but short-chain PFSAs were similar to PFOS with respect to bioaccumulation.

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